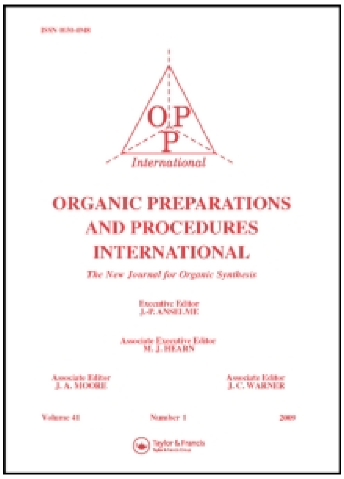

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THE CHEMISTRY OF 1,3-DIOXIMES. A BRIEF REVIEW

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THE CHEMISTRY OF 1,3-DIOXIMES. A BRIEF REVIEW

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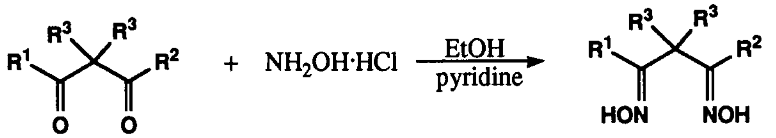
INTRODUCTION

It is well known that oximes have very interesting reactivity and are often used as intermediates for the preparation of a great variety of compounds.[1,2] Oximes and their derivatives have found wide use, for example, as anticancer agents, as dyes and bacteriostatic agents. There is also a large number of oximes with other important practical applications, such as photographic sensitizers and developers, vulcanization accelerators in the rubber industry and as valuable intermediates in synthesis. Therefore, a great variety of compounds such as nitriles, amines, substituted amides, hydroxylamines, α-aminoalcohols, nitrones and nitro compounds can be produced from oximes. They can also serve as precursors in the synthesis of a number of heterocycles such as aziridines, furazans, benzisoxazole *N*-oxides, quinazoline-3-oxides, pyrazole and pyrazoline 1,2-dioxides. The successful application of oximes and their use as materials in synthetic chemistry stems from their structure and their configuration and especially from the appropriate combination of oximino group with a variety of functional groups as amino, hydroxyl, oximino and others. An interesting case of this is that of dioximes. The presence of two oximino groups in a molecule in appropriate positions allows for the formation of interesting heterocycles by interaction of the functional groups. Attention has been focussed mainly on the 1,2-dioximes, whose chemistry has been reviewed in 1964.[3] Nevertheless, quite a number of papers about other types of dioximes has been published. An important member of this class of molecules is the 1,3-dioximes, and they form the subject of this review which aims at presenting an integrated picture of their chemistry. This article attempts to detail all the published aspects about 1,3-dioximes, including their synthesis, configuration, physical and chemical properties as well as their applications.

I. SYNTHESIS

The formation of oximes is a common reaction in organic synthesis.[4] The most often used approach[5-11] in the formation of 1,3-dioximes is the treatment of the corresponding 1,3-dicarbonyl compounds with a relatively large excess of hydroxylamine hydrochloride in the presence of pyridine (Eq. 1). In most of the cases shown of Eq. 1, the corresponding 1,3-diketones (**1**) used for the preparation of dioximes **2** are alkylated at the 2-position in order to avoid formation oftautomers.[12-14] This tautomerization causes a great difficulty in the formation of nitrogen



1 **2**

a : $R^1 = R^2 = R^3 = H$
b : $R^1 = R^2 = Me, R^3 = H$
c : $R^1 = Me, R^2 = Ph, R^3 = H$
d : $R^1 = R^3 = Me, R^2 = H$
e : $R^1 = R^2 = R^3 = Me$
f : $R^1 = R^2 = Me, R^3 = Et$
g : $R^1 = R^2 = Me, R^3 = Ph$
h : $R^1 = R^2 = Me, R^3 = CH_2Ph$
i : $R^1 = R^3 = Me, R^2 = Ph$
j : $R^1 = R^2 = Ph, R^3 = H$
k : $R^1 = Ph, R^2 = H, R^3 = Me$
l : $R^1 = Ph, R^2 = Me, R^3 = Et$
m : $R^1 = R^3 = Ph, R^2 = Me$
n : $R^1 = R^3 = Ph, R^2 = Et$
o : $R^1 = R^2 = R^3 = Me$
p : $R^1 = R^2 = Ph, R^3 = Et$

derivatives. The equilibrium which lies well to the right because the enol is stabilized by internal hydrogen bonding unavailable to the keto form, has been studied by *Seltzer*[15] in 1981. It was found[16] that the enol content of acetylacetone (**1b**) is 76.4 % and that of benzoylacetone (**1c**) is 89.2%. The usual approach to overcome these difficulties is to treat the unsubstituted β-diketone with a two-fold equivalent of hydroxylamine in ethanol-water for a long period of time (e. g. fifteen days stirring at room temperature for the preparation of **2j**). The isolation of the β-dioxime is completed by the addition of water; however, the yields are low.

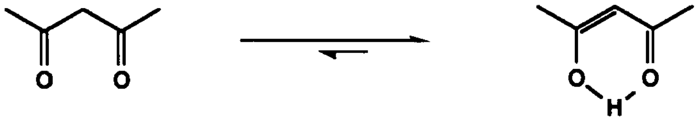
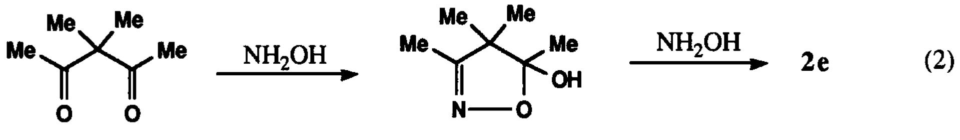
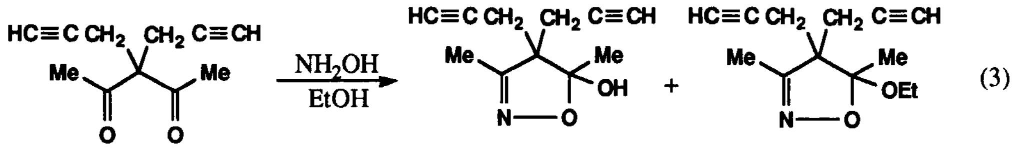


Fig. 1

Furthermore, in 1969 *Manning* and *Coleman* reported[7] that 3,3-disubstituted 2,4-pentanediones, *e.g.* **1e**, react with equimolar amounts of hydroxylamine to give good yields of 2-isoxazolin-2-ols (Eq. 2.). 3,4,4,5-Tetramethyl-2-isoxazolin-5-ol (**3**), prepared in this manner, underwent ring opening by treatment with an excess of hydroxylamine, forming 3,3-dimethyl-2,4-



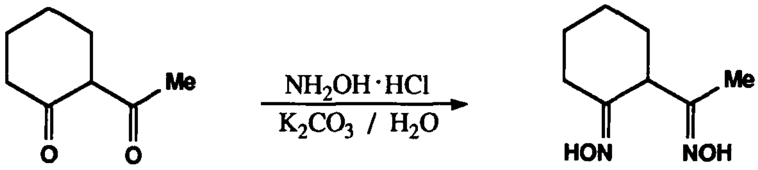
1e **3**



4 **5** **6**

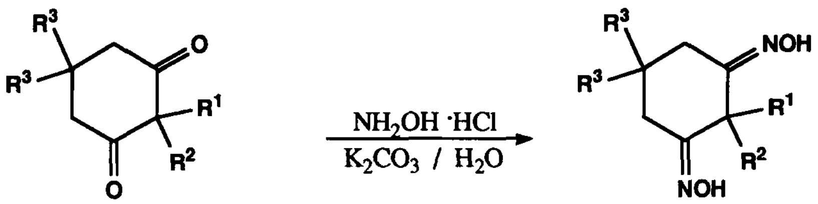
pentanedione dioxime **2e**. By contrast, all efforts to isolate a dioxime by hydroxylamine treatment of the 4,4-dipropargyl compound **5** failed. It has been observed[7] that treatment of **4** with hydroxylamine under various conditions afforded the 2-isoxazolin-5-ol **5** along with its ethoxy derivative **6** and not the dioxime, but no explanation was offered.

The synthesis of cyclic dioximes **9** and **10** has been known from an early date.[17] They are formed by treatment of the corresponding dicarbonyl compound **7** and **8** with hydroxylamine hydrochloride and potassium carbonate in water (Eqs. 3 and 4).



(4)

7 **9**

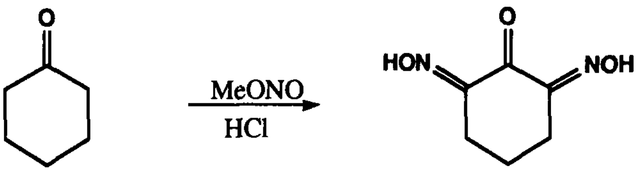


(5)

8 **10**

a: $R^1 = R^2 = H$, $R^3 = Me$ **b**: $R^1 = R^2 = R^3 = H$ **c**: $R^1 = Me$, $R^2 = R^3 = H$

The preparation of 2,6-dioximinocyclohexanone (**12**) was described first by *Borsche*,[18] then by *Treibs* and *coworkers*,[19,20] and later by *Ferris* and *coworkers*.[21,22] Treatment of cyclohexanone (**11**) with methyl nitrite in the presence of hydrochloric acid gave the dioxime **12** in about 75% yield (Eq. 6.)

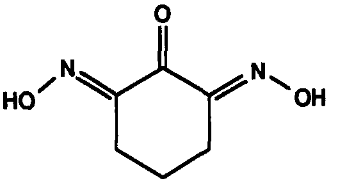


(6)

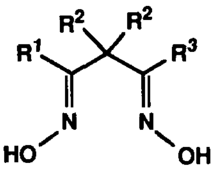
11 **12**

II. CONFIGURATION

There exist a few reports in the literature about the configuration of 1,3- dioximes.[8,22,24,25]. In 1960, *Ferris et al.*[22] established that dioxime **12** possesses the *anti* configuration. According to the work of *Taylor*[26,27] on the metal complexes of α-oximino ketones, it was assumed that **12** existed in the *anti* form. However, the configuration of **12** was established by a series of experiments. In one experiment, 2-oximinocyclohexanone was prepared and subjected to the Beckmann rearrangement. The action of benzenesulfonyl chloride and aqueous base gave a 71% yield of 5-cyanovaleric acid. In a second experiment, when 2,6-dioximinocyclohexanone **12** was treated with three equivalents of benzenesulfonyl chloride and base, a 50% yield of glutaronitrile was obtained. The fact that both reactions gave nitriles and not isonitriles [28] indicates that **12** and the other cyclic α-oximino ketones possess the *anti* configuration.

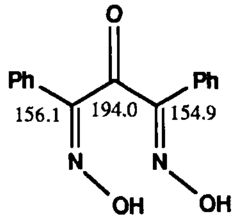


12 *anti*-

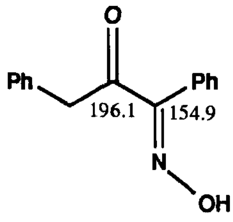


2 *anti*-

In 1980, *Gnichtel et al.*[8] reported that in the formation of 2,2-disubstitued 1,3-dioximes **2** (Eq. 1), only the *anti* isomer was isolated in all cases. The configuration was established by UV and ^{1}H nmr. Furthermore, the *amphi* configuration of 1,3-di(hydroximino)-1,3-diphenyl-2-propanone **13** was established by ^{13}C nmr.[8] The ^{13}C nmr spectrum showed that the two carbon atoms that bear the oxime groups were not equivalent. The peaks attributed to the *anti* oxime-C-atoms in **13** were analogous to those of 1(*E*)-hydroximino-1,3-diphenyl-2-propanone **14**.[29,30] Additionally, the phenyl rings in **13** were found to be not equivalent. Furthermore, the Beckmann rearrangement of **13** with thionyl chloride in chloroform leads to fragmentation. The isolation of benzonitrile, benzoic acid and the dianilide of oxalic acid supported the configuration of **13** as being *amphi*.



13 *amphi*-



14

Finally, it has been reported[25] that the alicyclic dioximes **10** (Eq. 5.) are formed as a mixture of the three inseparable stereoisomers.

III. SPECTROSCOPIC PROPERTIES

1. Infrared Spectra

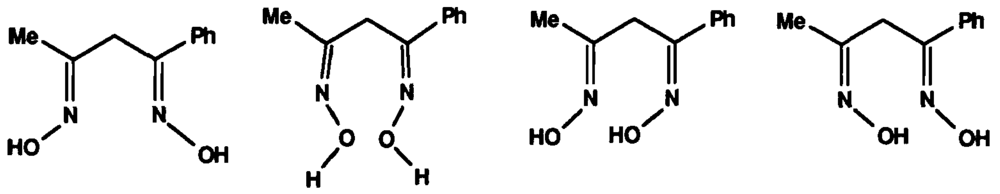
The IR spectra of 1,3-dioximes are characterized by the presence of absorptions at 3625-3150 and 1665-1620 cm^{-1}, attributed to the OH and to the C=N groups respectively.[6-10,24,31] It is interesting to note that the IR properties of some β-dioximato complexes such as of **2c** and **2j** with Cu(II) have been also reported.[24,31] Comparison of the IR data of the free ligand benzoylacetone dioxime (BADO, **2c**) with those of the corresponding complex Cu(II)-(BADO)$_2$, led to the establishment of the pseudoaromatic conjugated system in the complex chelate, as well as the existence of hydrogen bonding in both ligand and complex species.[24]

2. Ultraviolet Spectra

The UV spectra of some 1,3-dioximes have been reported,[8,31] along with those of Cu(II)- and Ni(II)- β-dioximato complexes.[31,32] Attention has been paid to the UV spectra of dioximes **2p** and **2j** that are characterized by absorptions at 230 and 223 nm respectively, typical for the *anti*-phenyl conjugated oxime.[33]

3. Nuclear Magnetic Resonance Spectra

In 1975, *Ben-Bassat* and his *coworkers* described[24] the ^{1}H nmr spectra of acetylacetone dioxime **2b** and benzoylacetone dioxime **2c**. The resonance line of the protons of the methylene protons appear at a lower than expected position. For example, in the ^{1}H nmr spectrum of **2c** in D_2O they appear at δ 3.52, whereas the chemical shift for the methyl group adjacent to the oxime group is at δ 2.28. Furthermore, the ^{1}H nmr spectrum of **2b** in $CDCl_3$ shows a peak at δ 1.6 for the methyl groups, whereas this signal appears at δ 2.04 when D_2O was used as the solvent. The non-equivalence of the methylene protons results in a typical pattern at δ 6.25 and 6.37. This pattern indicates the possibility of restricted rotation of the aliphatic chain and it is attributed to the existence of an equilibrium between open chain (*anti*, *syn*) and cyclic (*amphi*) isomers in solution. In addition, the peaks at δ 3.75 and 3.98 were assigned to the methylene hydrogens of the *anti* and *syn* forms, respectively. A broad peak at δ 5.6 is probably due to the NH proton of the nitrone form of the oxime group or the hydrogen of the NHO hydrogen bond of the *amphi* form. However, there is no nmr evidence for the existence of isomeric mixtures in the case of **2b** in D_2O. The ^{1}H nmr spectra of some more 1,3-dioximes have been reported.[8-11]



anti- *syn*- **2c** *amphi*-

Fig. 2

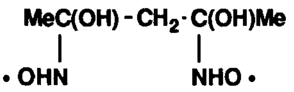
4. Mass Spectra

The mass spectra of 1,3-dioximes first received attention in 1987 when a study of the electron impact fragmentation of aliphatic and alicyclic 1,3-dioximes was reported.[34] A consistent fragmentation pattern was observed in the spectra of 2,2-disubstituted 1,3-dioximes **2**, **10** and **12**.[34] The fragmentation of **2** is characterized by the presence of peaks at m/z $[M]^+$, $[M\text{-}16]^+$, $[M\text{-}17]^+$ and $[M\text{-}31]^+$ corresponding to the molecular ion, to the loss of an oxygen, of a hydroxy radical and of an oximino radical from the molecular ion respectively. Alternative fragmentations could be rationalized by skeletal rearrangements incorporating the substituents. No primary dehydration of the molecular ion was observed, in contrast with the previously reported mass spectra for 1,2-dioximes.[35] Furthermore, the main fragmentations of alicyclic 1,3-dioximes **10** and **12** conform to two types: (i) decomposition involving the two functional moieties or their interaction and (ii) decomposition incorporating the cyclohexane ring.

5. Electron Paramagnetic Resonance Spectra

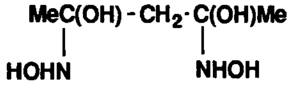
In 1969, *Edge and Norman* reported[36] that when freshly mixed solutions of titanium(III) chloride, hydroxylamine and acetylacetone (**1b**) were passed through the cavity of an esr spectrometer, the spectrum of a radical of type **15** was observed. Evidently, the adduct **16**, which is a precursor to the oxime, was both formed and oxidized exceptionally rapidly. The radical **15** was also formed by the addition of the hydroxyl radical to the dioxime at both pH = 1 and 9. The analogous radical **17** was formed by the addition of the amino radical to the dioxime.

The coupling constant for the radical **15** derived from solutions at pH = 6 was 13.2 whereas, for the radical **17** the coupling constant was 12.4 and 2.2.



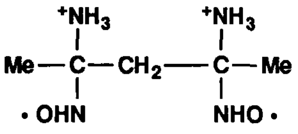
$$\mathrm{Me}\underset{\underset{\bullet\,\mathrm{OHN}}{|}}{\mathrm{C}}(\mathrm{OH})-\mathrm{CH_2}\cdot\underset{\underset{\mathrm{NHO}\,\bullet}{|}}{\mathrm{C}}(\mathrm{OH})\mathrm{Me}$$

15



$$\mathrm{Me}\underset{\underset{\mathrm{HOHN}}{|}}{\mathrm{C}}(\mathrm{OH})-\mathrm{CH_2}\cdot\underset{\underset{\mathrm{NHOH}}{|}}{\mathrm{C}}(\mathrm{OH})\mathrm{Me}$$

16



$$\mathrm{Me}-\overset{\overset{^{+}\mathrm{NH_3}}{|}}{\underset{\underset{\bullet\,\mathrm{OHN}}{|}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\overset{^{+}\mathrm{NH_3}}{|}}{\underset{\underset{\mathrm{NHO}\,\bullet}{|}}{\mathrm{C}}}-\mathrm{Me}$$

17

Fig. 3

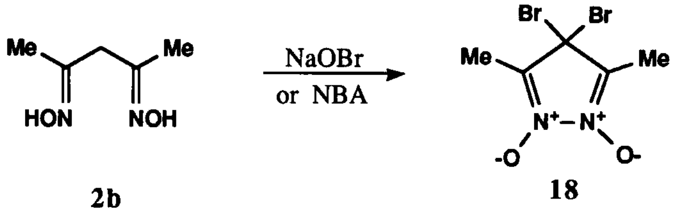
IV. REACTIVITY

1. Oxidation

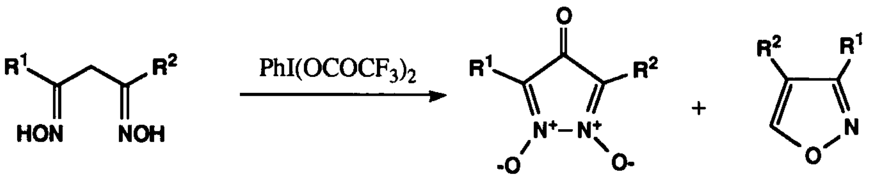
There exist a number of reports on the oxidative cyclization of 1,3-dioximes with a variety of oxidizing agents, such as sodium hypobromite, phenyliodoso bistrifluoroacetate (PIT), lead tetraacetate (LTA) and sodium hypochlorite.[9-11,37-40]

Oxidation of dioxime **2b** by NaOBr gave a moderate yield of the heterocyclic *N*-oxide **18**. Superior results were realized when the reaction was modified by using *N*-bromoacetamide (NBA) in place of NaOBr (Eq. 7.).[38] Treatment of the dioximes **2(b, c, j)** with PIT leads to the formation of 4-

oxo-2*H*-pyrazole 1,2-dioxides **19** and to the corresponding 3,5-disubstituted isoxazoles **20** (Eq. 8).[39]

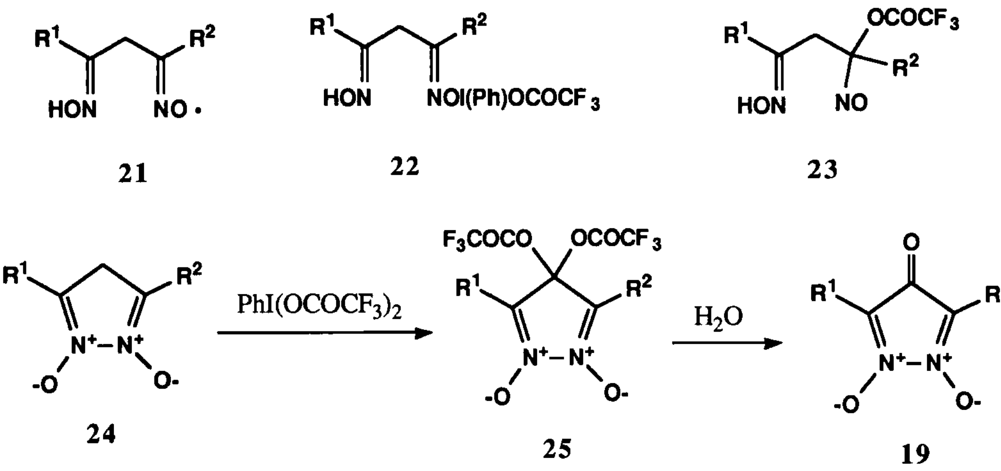


2b **18** (7)



2 (b, c, j) **19** **20** (8)

Several possibilities have been proposed with regard to the mechanism of the above reaction: the intermediate has been suggested to be an iminoxy radical (**21**) obtained by abstraction of H• or an iodine(III) derivative (**22**), or a *gem*-nitrosotrifluoroacetate (**23**). Such intermediates are known to be formed from simple oximes by eventual release of iodobenzene and trifluoroacetic acid.[39] These may further be converted into **24**, which reacts with more PIT and gives **25**, which is finally hydrolysed, probably during work-up (Fig. 4.).

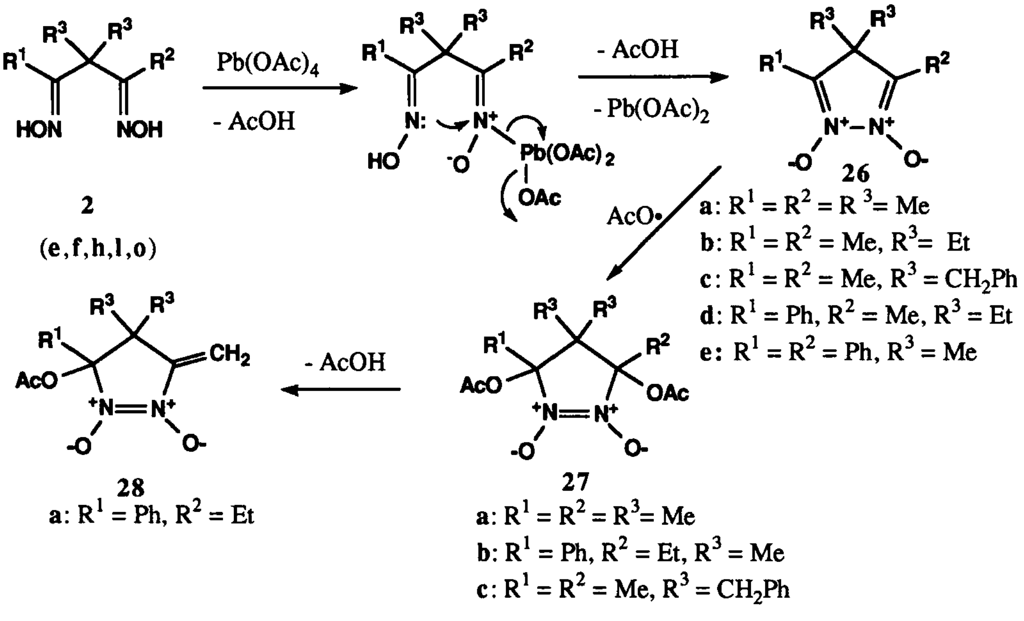


21 **22** **23**

24 **25** **19**

Fig. 4

Oxidation of **2** with LTA resulted mainly in pyrazole dioxides **26**.[9,10] In most cases acetoxylated pyrazoline 1,2-dioxides **27** and **28** were also produced in substantial quantities, along with a number of side-products (Fig. 5). Although the reasons for the preferential formation of pyrazole 1,2-dioxides rather than the acetoxylated compounds are uncertain, it appears that the



2
(e,f,h,l,o)

26
a: $R^1 = R^2 = R^3 = Me$
b: $R^1 = R^2 = Me$, $R^3 = Et$
c: $R^1 = R^2 = Me$, $R^3 = CH_2Ph$
d: $R^1 = Ph$, $R^2 = Me$, $R^3 = Et$
e: $R^1 = R^2 = Ph$, $R^3 = Me$

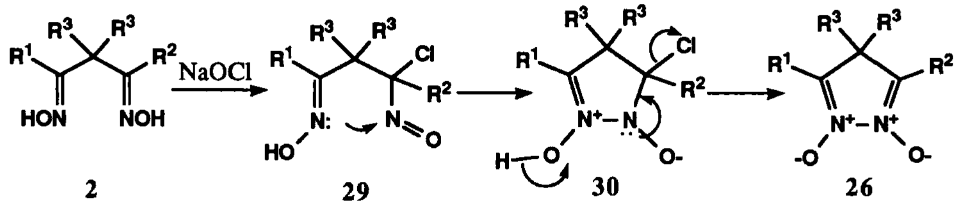
27
a: $R^1 = R^2 = R^3 = Me$
b: $R^1 = Ph$, $R^2 = Et$, $R^3 = Me$
c: $R^1 = R^2 = Me$, $R^3 = CH_2Ph$

28
a: $R^1 = Ph$, $R^2 = Et$

Fig. 5

substituents R^2 influence the progress of the reaction. Moreover, alkyl or aryl groups adjacent to the C=NOH moiety have also some effect. The formation of *N*-oxides **26** is thought to be an intermediate step in the acetoxylation, which results from the presence of acetoxyl radicals produced from LTA in the course of the reaction. It is envisaged that **28** results from the elimination of a molecule of acetic acid from **27** (Fig. 5).

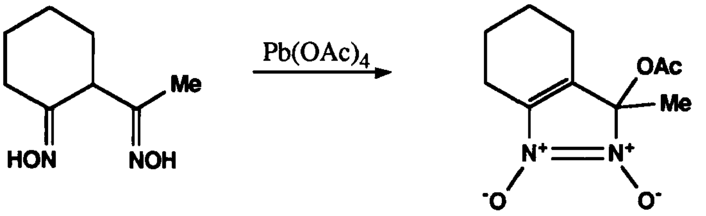
Subsequently, the reaction conditions and the yields of the heterocycles **26** were optimized using commercially available sodium hypochlorite solution.[11] The use of this oxidant is advantageous in that it requires simple and mild reaction conditions, easy work-up and gives rather respectable yields of **26**. The low cost of the reagent adds to the synthetic value of the method. A plausible reaction pathway for the oxidative cyclization of 1,3-dioximes **2** is depicted in Eq. 9.



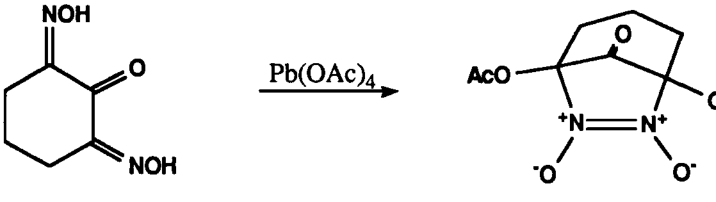
2 29 30 26

(9)

In addition, a few alicyclic 1,3-dioximes have been oxidative cyclized to the corresponding pyrazole *N*-oxides (Eqs. 10 and 11).[9] It is quite likely that the LTA oxidation mechanism proposed for the aliphatic 1,3-dioximes is also operative in cases where the =NOH is attached to a carbocyclic ring.

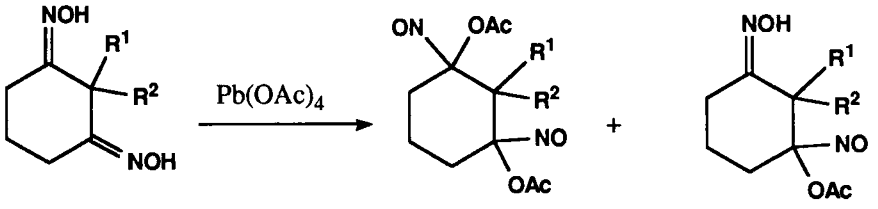


9 31 (10)

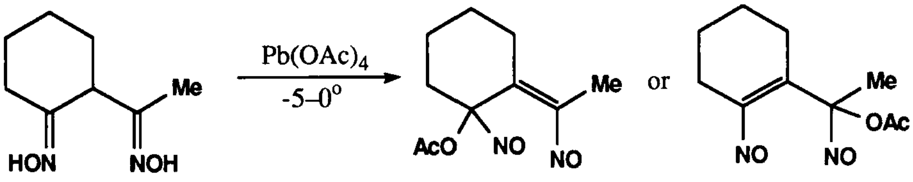


12 32 (11)

Recently, it has been reported [41] that alicyclic 1,3-dioximes **10** lead to the formation of nitrosoacetates **33** and **34** upon treatment with LTA (Eq. 12). It has also been noticed that when the reaction takes place at -5 to 0° the *gem*-nitrosoacetoxy compound, whose structure could be **35** or **36**, was isolated from the LTA oxidation of **9** (Eq. 13). The formation of either the *gem*-nitrosoacetates **33**, **34** and **35** (Eqs 12 and 13) or the heterocyclic 1,2-dioxides **31** and **32** (Eqs. 10 and 11) is presumably influenced by the conformational effects of the cyclohexane ring. Furthermore, in the oxidation of **9** the isolated products **31** and **35** were obviously the result of free rotation about the exocyclic C-C bond. Besides, in the case of **12** the valence-bond isomeric *gem*-nitrosoacetate of **32** might be the initially formed intermediate, which being unstable would undergo cyclization to the corresponding heterocycle **32**.



10 33 34 (12)

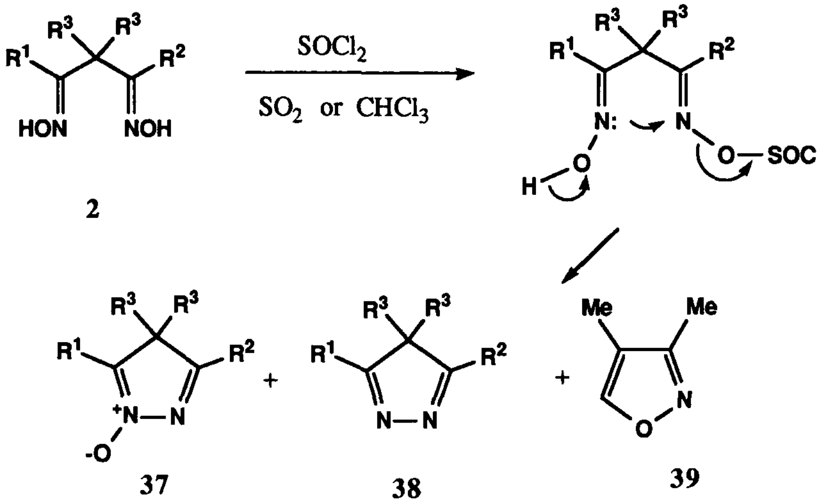


9 35 36 (13)

Finally, an esr study of the oxidation of some 1,3-dioximes by LTA or $Ce(NH_4)_2(NO_3)_6$ were reported in 1984.[42] Iminoxyl and nitroxyl radicals were detected, and the esr spectra were interpreted. No evidence was found for bisiminoxyl radicals.

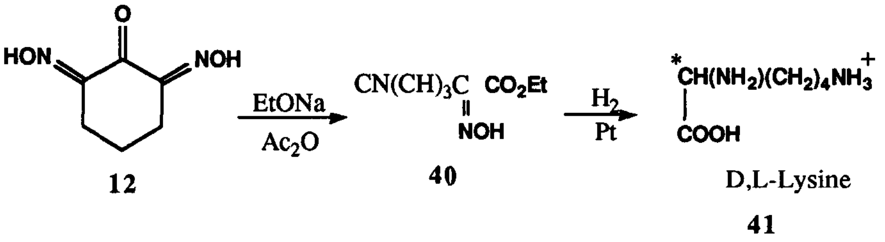
2. Beckmann Rearrangement

In 1966, *Gnichtel* and *coworkers*, reported the reaction of 1,3-dioximes **2e** and **2f** with thionyl chloride in liquid sulphur dioxide at -60°.[6] The main products were the corresponding pyrazole 1-oxides **37**, along with minor amounts of the parent pyrazoles **38** as by-products (Eq. 14). Later, *Gnichtel et al.*[8] found that a much cleaner reaction resulted when the 1,3-dioximes **2** were treated with thionyl chloride in chloroform at room temperature; the *N*-oxides **37** are the only products. The importance of substitution at the 2-position of the dioximes was demonstrated by the isolation of isoxazole **39** as the sole product, when this position is unsubstituted as in **2b**, evidently owing to tautomerization of the latter.



(14)

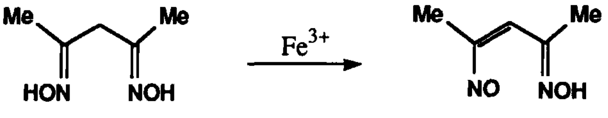
Furthermore, *Ferris'* group[21,22] used the Beckmann rearrangement of 2,6-dioximinocyclohexanone **12** to achieve a synthesis of lysine **41** (Eq. 15.). The sodium salt of **12** was treated in ethanol with acetic anhydride to effect Beckmann rearrangement to ethyl 5-cyano-2-oximinovalerate **40**. Hydrogenation over Raney nickel with a basic co-catalyst and subsequent hydrolysis afforded *DL*-lysine monochloride in 63% overall yield from cyclohexanone. A less successful application of the sequence to cyclopentanone affords *DL*-ornithine in overall yield of 21%.



(15)

3. Complex Formation

Lloyd, McDougall and *Wasson*[43] reported in 1965 that the attempted reduction of **2b** by hydrazine-Raney nickel formed nickel complexes instead of amines. Later, in 1970, *Ben-Bassat et al.*[31] studied the reaction between Fe(III) and acetylacetone dioxime (AADO, **2b**) by potentiometric, polarographic and spectrophotometric methods. The Fe(III) in aqueous solution oxidize one AADO molecule to 2-nitrosopent-2-en-4-one oxime (NPO) **42** (Eq. 16.). The latter forms a water-soluble red colored complex with Fe(III). The elemental analysis of the solid complex was found to be consistent with the compound $FeO(NPO)_2(OH)$. It has also been reported that $k_{redox} = 1.72 \times 10^{-1}$ min^{-1} and $k_{complex} = 5.13 \times 10^{-2}$ min^{-1}. Furthermore, the formation of the complexes of Cu(II) with BADO **2c** have been reported[24,31] to be of the type $Cu(BADO)^*_2$, where BADO* = oxidized BADO.



2b **42** (16)

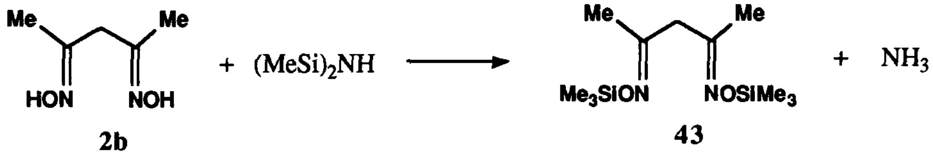
Finally, in 1978 *Gottstein* and *Keller*[44] reported that treatment of several alkyl and aryl substituted 1,3-dione dioximes, such as acetylacetone dioxime **2b**, with Ni(II), Pd(II) and Pt(II) in aqueous or alkaline solutions, gave two kinds of complexes: (i) those with stoichiometry metal/ligand = 1/1 and (ii) bis(1,3-dionedioximato)metal(II) complexes. None of the isolated solid compounds showed any sign of appreciable intermolecular metal interactions. An attempt to enhance intermolecular interations by oxidizing the compounds lead to the destruction of all the complexes.

4. Other Reactions

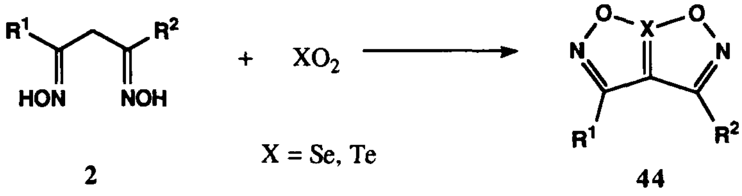
There exist several reports describing the involment of 1,3-dioximes in several reaction types as it is outlined below. In 1969, *Taylor et al*[45] reported the synthesis of a pyrazine-*N*-oxide starting from the 1,3-dioxime of type HC(NOH)COCH(NOH). This reaction was a part of pterin-6-carbaldehyde synthesis. The synthesis of isoxazoles has been reported and consists of refluxing 1,3-dioximes in either acetic or sulphuric acid.[46-49] Isoxazoles can also be by-products in some oxidation reactions of 1,3-dioximes, *e.g.* compounds **20** and **39**.

Cyclohexane-1,3-dione dioxime hydrochloride was prepared in 1970.[50] It has been found by nmr and ir studies that the salt is the enamine form of the oxime. Furthermore, the salts of 2-methylcyclohexane-1,3-dione dioxime **10c**, 5,5-dimethylcyclohexane-1,3-dione dioxime **10a** and acetylacetone dioxime **2b** have been prepared and have the same type of structure.

In 1976, *Kule* and *coworkers*[51] reported, the reaction of some dioximes with methylsilazanes. Acetylacetone dioxime **2b** gave the corresponding O,O'-bis-trimethylsilylated dioxime **43** upon treatment with hexamethyltrisilazane (Eq. 17). In 1979, *Perrier* and *Kalle*[52] described the synthesis of 1,6-dioxa-6a-seleno-2,5- diazapentalenes **44** and their sulfur- and tellurium-containing homologs by treatment of 1,3-dioximes **2** with XO_2 (Eq. 18).

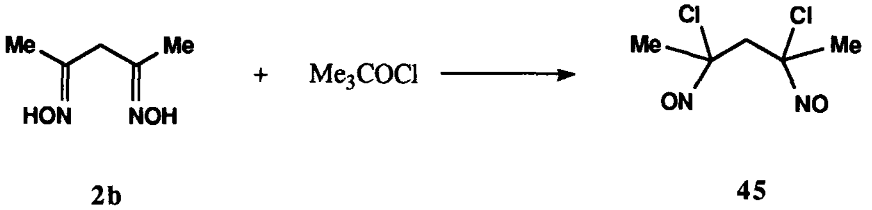


(17)



(18)

Finally, acetylacetone dioxime **2b** when treated with *tert*-butyl hypochlorite in 1,1,2,2-tetrafluoro-1,2-dichloromethane yielded 2,4-dinitrosopentane (**45**) (Eq. 19) that can be converted to a vulcanizate.[53]



(19)

V. APPLICATIONS

1,3-Dioximes have found applications in a rather wide field. However, most of the references are about acetylacetone dioxime (**2b**). Thus, **2b** is used as a photographic development accelerator.[54] It reduces fogging and it does not adversely effect the granularity of the developed film. Furthermore, in 1985, it has also been reported by *Fuji Photo Film*[55] that silver halide photographic materials containing blocked photographic useful reagent-releasing compounds are processed in the presence of oxime type compounds. Thus, the fog inhibitor-releasing rate of special compounds is increased by the presence of oximes. The photographic material consists of a support and a silver halide emulsion layer containing an oxime of formula $R^1C(NOH)(CH_2)_nC(NOH)R^2$ where R^1 and R^2 are H, C_{1-4} alkyl, aryl, carboxyl or heterocyclic groups and n = 0, 1, or 2.[56]

In 1982, some photothermographic and photosensitive compounds were synthesized[57] and became colored upon oxidation. It has been found that acid-type color formation promoting agents are Co(III) complexes with chelating agents of the formula $R^1C(NOH)(CH_2)_nC(NOH)R^2$ where R^1 and R^2 = alkyl, aryl and n = 0-3. Thus, photothermographic film coated with this material gives a high-quality image.

In addition, organic polymers are reported to be crosslinked with polyfunctional chloronitroso compounds.[53] Thus, acetylacetone dioxime (**2b**) is oxidized to **45** (Eq. 19) which, by subsequent treatment with polyethylene, is then converted to an odorless and completely gelled vulcanizate. The latter is substantially insoluble in carbon tetrachloride and chlorobenzene. Its physical properties, such as tensile strength and elongation, have been reported.

1,3-Dioximes also find application in analytical chemistry. A sensitive detection test for both Ni and Co in the presence of each other, requiring no previous separation and using acetylacetone dioxime (**2b**) as the reagent is known.[58] The complex of Ni with the dioxime is extracted into chloroform at pH = 7-8. The Co chelate remains mostly unextracted under similar conditions and shows a strong reddish-brown color in alkaline solutions at pH = 11. For positive results, the sample test solution must contain at least 0.6 mg of Ni and 0.6 mg of Co per ml.

It has been reported[59] that the addition of an aliphatic dioxime in an amount equivalent to 1-4% by weight of the total propellant mass, improves the low-temperature ignitability by lowering of the pressure exponent. Suitable oximes have the formula of $R^1C(NOH)CH_2C(NOH)R^2$, where R^1, R^2 = Me, Et or H.

Finally, it is worthwhile to note the importance of 1,3-dioximes as precursors in the synthesis of various significant organic molecules as described above.

VI. CONCLUSIONS

The versatility of 1,3-dioximes has been illustrated in the results presented in this review. Their synthesis and configuration as well as their physical properties, their reactivity and use have been discussed. Their ^1H nmr spectra with comparison to those of the corresponding complex derivatives seem to be quite interesting. Existence of hydrogen bonds and of *anti, syn, amphi* forms were established.[24] However, no ^{13}C nmr study has been published. Their reactivity is influenced mainly by the presence of substituents at the carbon between the oximino groups. One of the most interesting reaction which is influenced by these substituents is their oxidative cyclization, which yields various heterocycles such as pyrazoles, pyrazole *N*-oxides and 1,2-dioxides and isoxazoles.[40]

Finally, it is worthwhile noticing that the applications of 2,2-disubstituted 1,3-dioximes have received no attention, whereas 1,3-dioximes bearing a CH_2 group between the two oximino functions found wide applications in various fields.[54-59] An important fact of all 1,3-dioximes, is that they can lead to derivatives either cyclic (heterocyclic[6-11,37-40,45-49,52] and alicyclic[41]) or acyclic compounds.[22,53]

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